Reducing user-interaction in the processing of electron energy-loss spectra

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Background
Conventional processing of electron energy-loss spectra (EELS) relies heavily on user-determined parameters, like for instance location and width of a background window, or choice of fine structure region. This makes results operator-dependent, more subjective and harder to reproduce.
Here we introduce a model-based processing of EEL spectra that relies on a linear model for which physical constraints are derived and subsequently imposed with the aid of quadratic programming. The model's linearity ensures fast convergence and the absence of local optima. Since the model includes all relevant EELS-features---background, atomic cross sections, fine structure, and multiple scattering---minimal user-interaction is required.

Methods
The background is described as a sum of 4 to 5 power-laws with fixed exponents ranging from -1 to -5. During the fit the coefficients are subjected to constraints that ensure non-negativity, monotonous descent and convexity. This background was proven to hold for energy ranges up to 1500 eV and to be superior to the conventional power-law background model [1].

The atomic cross sections are taken from a data base [2] that contains all edges of all elements up to atomic number 108. They were obtained from numerical relativistic solutions to the Dirac equations.

The fine structure is modeled as a quadratic spline with either linearly or quadratically spaced sample points. Working out the Bethe sum rule, assuming independent atomic shells and the dipole approximation, shows that the fine structure must have a weighted sum of zero. This constraint, too, is enforced through quadratic programming.

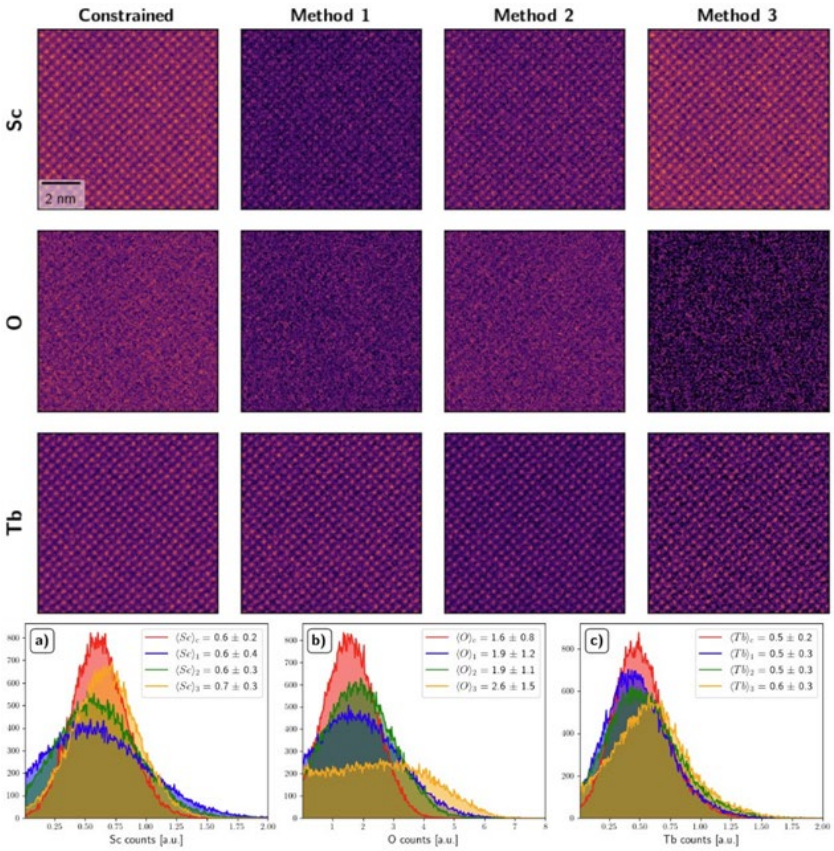
Results
In the figure the elemental maps of a TbScO3 sample are shown, in order to compare our approach to three alternative methods:
1. Unconstrained fit, with fine structure, no energy ranges excluded from fit.
2. Unconstrained fit, without fine structure, fine structure region excluded from fit.
3. Conventional approach: background region in front of each edge, background extrapolated and subtracted.

These 3 methods require a substantial amount of user choices, which we made to the best of our abilities. In comparison, our unsupervised approach yields the highest-contrast elemental maps, while offering a better precision, as demonstrated in the concentration histograms in the figure.

Conclusions

Imposing physical constraints on the EELS model through quadratic programming---in this case non-negativity, monotonous descent and convexity for the background, and the Bethe sum rule for the fine structure---greatly improves the quality of the result and removes most of the user-dependent input from the fitting process.

Graphic:



Keywords:

EELS; Constrained optimization; Background; Fine-structure

Reference:

[1] W. Van den Broek et al. Ultramicroscopy 254 (2023) p. 113830
[2] Z. Zhang et al. https://zenodo.org/records/7729585